

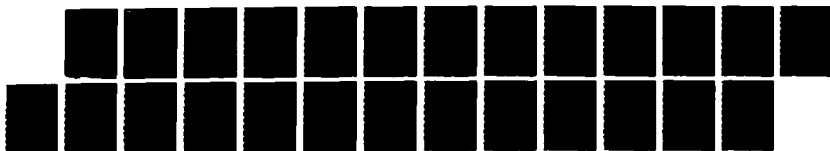
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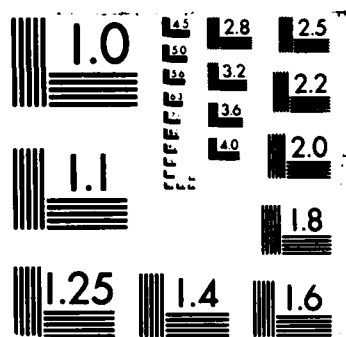
SYNTHESIS OF NOVEL FLUORINE COMPOUNDS: NEW EXPERIMENTAL 1/1
CHALLENGES IN ELE (U) TEXAS UNIV AT AUSTIN DEPT OF
CHEMISTRY R J LAGOW 30 APR 87 AFOSR-TR-87-0600
AFOSR-82-0197

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FINAL REPORT

AFOSR-TR-87-0600

to

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Washington, DC 20332-6448

SYNTHESIS OF NOVEL FLUORINE COMPOUNDS: NEW EXPERIMENTAL

CHALLENGES IN ELEMENTAL FLUORINE CHEMISTRY

Grant Number AFOSR-82-0197

Presented by

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19. ABSTRACT (Continue on reverse if necessary and identify by block number) <p>This final report covers the most recent progress in this research program which has had ongoing support from AFOSR for the past ten years including the synthesis of perfluoropolyethers via hydrocarbon polyesters, the synthesis of branched perfluoro ethers, the synthesis of the first perfluoro crown ethers and the process for partial fluorination of gas separation membranes.</p>					
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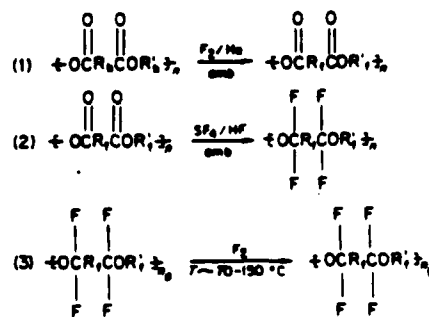
Over the last several years our research program has been heavily involved in developing the technology previously mentioned which is now being focused upon commercially to established broad based routes to perfluoropolyethers, one of the most exotic and important classes of high performance materials to be developed over the last twenty years. Our original route involved the very straightforward controlled elemental fluorination of hydrocarbon polyethers, the simplest process being the fluorination of the hydrocarbon poly(ethylene



These direct fluorination techniques have markedly increased the number of perfluoropolyether structures available for study; however, there are only 13 commercially available hydrocarbon polyether precursors.

We have developed a new synthetic method which we consider to be truly general and which will open synthetic routes to literally hundreds of different perfluoroether and perfluoropolyether structures.⁴ This synthetic technique involves the conversion by direct fluorination of hydrocarbon polyesters to perfluoropolyesters followed by treatment with sulfur tetrafluoride to produce new perfluoropolyethers and in some cases perfluoropolyether esters which can be hydrolyzed to produce functional fluorocarbon polyethers.

General Synthetic Scheme

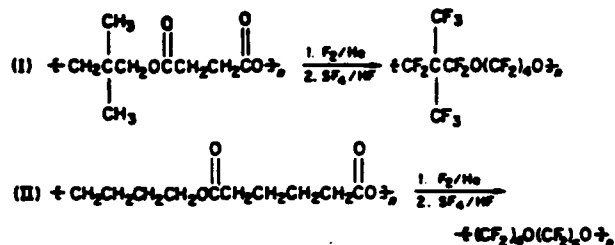


$n_1 \geq n_2$



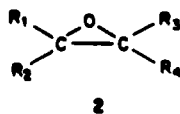
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The first reported syntheses in this manner were the conversion of poly(2,2-dimethyl-1,3-propylene succinate) (I) and poly(1,4-butylene adipate) (II) to novel branched and linear perfluoropolyether structures, respectively:

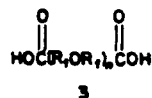


These new methods offer a number of significant and important advantages. The first advantage with this technique is that it is possible to prepare perfluoropolyethers containing more than two sequential carbon atoms in the perfluoropolyether backbone between adjacent oxygen sites. In the tetrafluoroethylene oxide and hexafluoropropylene oxide technology (i.e., polymerization of vinyl monomers and vinyl epoxides), one is limited to repeating two carbon-ether chains. A second important advantage is that perfluoropolyethers with unsymmetrical repeating units (alternating copolymers) are available (AOBOAOB) whereas with vinyl epoxides, other than random copolymers, one must have repeating AOA structures. A third advantage is that this technique also is capable of producing highly branched ethers which have elastomeric properties and fluids of higher thermal stability.

It is clear that if one considers as a class vinyl epoxides of the form of structure 2 where R groups are large, such as more than two trifluoromethyls or structures much more exotic, polymerization would be hampered markedly by the steric bulk of certain R groups, leading to a low molecular weight materials.



In many cases the synthesis of certain vinyl-substituted epoxide monomers would be extremely difficult or impossible even if polymerization were not a problem. A fourth and very important advantage with this method is the ease with which one can leave ester units in the high polymer and subsequently base hydrolyze to produce difunctional fluorocarbon polyesters of lower molecular weight.



Functionalization of fluorocarbon polyethers is exceedingly difficult with conventional technology and often involves many steps and extremely high costs. An important effect observed when nonstoichiometric amounts of SF_4 are used is illustrated in Figure 1. Normally a 2-fold excess of SF_4 is necessary to obtain

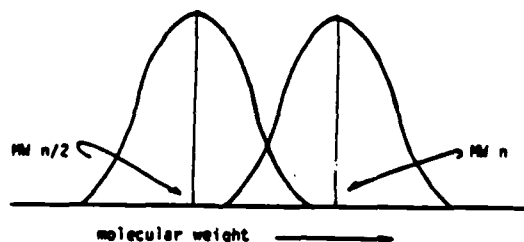


Figure 1. Gaussian distribution of difunctional perfluoropolyether molecular weights produced with n and $n/2$ mol of SF_4 . Both samples are hydrolyzed to produce the diacids after treatment with SF_4 .

the high molecular weight nonfunctional polymer. As illustrated, if less than stoichiometric amounts of SF_4 are used, one obtains different Gaussian distributions of molecular weights, indicative of the average distance between the ester units left in the macromolecule. By varying the SF_4 used, it is possible to shift the average molecular weight distribution at will. This technology makes available a very low-cost route to important new fluorocarbon surfactants and intermediates.

There are some 350 commercially obtainable linear hydrocarbon polyesters; thus the sulfur tetrafluoride-to-ether conversion technique is very broadly

applicable to produce many novel perfluoroether structures. There are also over 750 hydrocarbon polyester structures prepared and characterized in the literature, allowing this technique almost total structural flexibility.

A new development in the perfluoroether field enables the synthesis of a number of surfactants and perfluoroesters containing ether linkages. This extends the technique and the manuscript establishes a number of new synthetic routes to surfactants.⁶ There is already industrial interest in this new technology.

SPECTRAL ASSIGNMENTS OF COMPOUNDS FROM 0% SF₆ REACTION

Compound	Highest m/e in mass spec	¹⁹ F NMR (rel. CFC1 ₃)	¹ H NMR (rel. TMS)
(CF ₂ CO ₂ CH ₃) ₂	159 P-CO ₂ CH ₃	-120.6	63.91
(CO ₂ CH ₃) ₂	59 P-CO ₂ CH ₃	-	63.89
(CF ₂ CO ₂ H) ₂	145 P-CO ₂ H	-120.3	61.43
(CO ₂ H) ₂	45 P-CO ₂ H	-	59.00

SPECTRAL ASSIGNMENTS OF COMPOUNDS FROM 25% SF₆ REACTION

Compound	Highest m/e in mass spec	¹⁹ F NMR	¹ H NMR
(CF ₂ CO ₂ CH ₃) ₂	159 P-CO ₂ CH ₃	-120.6	63.96*
(CO ₂ CH ₃) ₂	59 P-CO ₂ CH ₃	-	63.96*
H ₃ CO ₂ CCF ₂ OCF ₂ CF ₂ CF ₂ CO ₂ CH ₃	275 P-CO ₂ CH ₃	a -77.8 b -83.7 c -126.8 d -119.1	63.96*

*Average chemical shift of CH₃'s

SPECTRAL ASSIGNMENTS OF COMPOUNDS FROM 50% SF₆ REACTION

Compound	Highest m/e in mass spec	¹⁹ F NMR	¹ H NMR
H ₃ CO ₂ CCF ₂ OCF ₂ CF ₂ CF ₂ CO ₂ CH ₃ a b c d	275 P-CO ₂ CH ₃	a -77.3 b -84.2 c -127.0 d -119.0	63.93*
H ₃ CO ₂ CCF ₂ CF ₂ CF ₂ O(CF ₂) ₂ OCF ₂ CF ₂ CF ₂ CO ₂ CH ₃ a b c d c b a	491 P-CO ₂ CH ₃	a -119.0 b -127.0 c -84.2 d -88.7	63.93*
H ₃ CO ₂ CCF ₂ OCF ₂ CF ₂ CF ₂ CF ₂ OCF ₂ CO ₂ CH ₃ a b c c b a	391 P-CO ₂ CH ₃	a -77.3 b -84.2 c -125.5	63.93*
H ₃ CO ₂ CCF ₂ OCF ₂ CF ₂ CF ₂ CF ₂ OCF ₂ CF ₂ OCF ₂ CF ₂ CO ₂ CH ₃ a b c c b d d b e f	607 P-CO ₂ CH ₃	a -77.3 b -84.2 c -125.5 d -88.7 e -127.0 f -119.0	63.93*

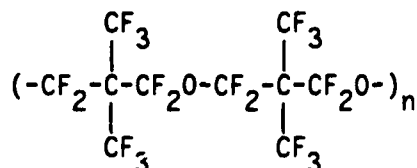
*Average chemical shift of CH₃'s

SPECTRAL ASSIGNMENTS OF COMPOUNDS FROM 100% SF₆ REACTION

Compound	Highest m/e in mass spec	¹⁹ F NMR	¹ H NMR
(H ₃ CO ₂ CCF ₂ OCF ₂ CF ₂ CF ₂ OCF ₂) ₂ a b c c b d	723 P-CO ₂ CH ₃	a -78.0 b -83.3 c -125.3 d -88.6	63.94*
(H ₃ CO ₂ CCF ₂ CF ₂ CF ₂ OCF ₂ CF ₂ OCF ₂ CF ₂) ₂ a b c d d c e	823 P-CO ₂ CH ₃	a -119.3 b -126.6 c -83.3 d -88.6 e -125.3	63.94*
H ₃ CO ₂ CCF ₂ O(CF ₂ CF ₂ CF ₂ OCF ₂ CF ₂ O) ₂ CF ₂ CF ₂ CO ₂ CH ₃ a b c c b d d b e f	939 P-CO ₂ CH ₃	a -78.0 b -83.3 c -125.3 d -88.6 e -126.6 f -119.3	63.94*

*Average chemical shift of CH₃'s

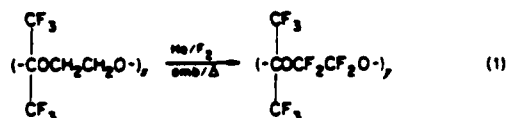
A number of really intriguing perfluoropolyether structures have been prepared using this technique.⁴ For example, a manuscript is in preparation now on the following structure:



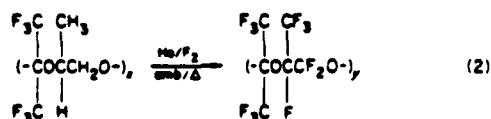
Note that this is a very interesting molecule structurally. It essentially contains perfluoro neopentyl (almost a perfectly spherical and inert fluorocarbon group) connected with a chain of very flexible oxygen hinges. The materials that we have prepared have a degree of polymerization around 150 and are extremely stable solids (decomposing about 420°C). This structure is much like a chain of pearls with the oxygen serving as the string and makes very little contact with a surface, for example in lubrication studies. This is thought to have potential as a solid lubricant and samples are under study in the National Aeronautics and Space Administration Lewis Research Center's Tribology Department. Efforts are underway to make even higher molecular weight species.

Another breakthrough in the synthesis of perfluoropolyethers involves the synthesis of branched perfluoropolyethers from copolymers based on hexafluoroacetone.⁷ Three new perfluoropolyether structures have been produced by fluorination of hexafluoroacetone copolymers with ethylene oxide-propylene oxide oxetanes:

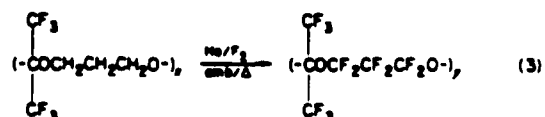
hexafluoroacetone/ethylene oxide copolymer



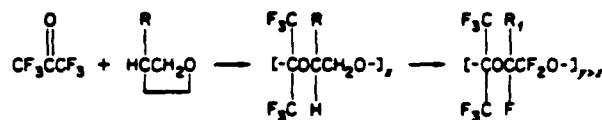
hexafluoroacetone/propylene oxide copolymer



hexafluoroacetone/oxetane copolymer



The general scheme of the polymerization process is as follows:



The physical properties of these new structures are still being evaluated but it should be noted that prior to our work there were available only Du Pont's homopolymer of hexafluoropropylene oxide and Montecatini Edison's polymerization of mixtures of oxygen and tetrafluoroethylene (to give two different structures). Therefore with the exception of various molecular weight ranges, before our work there were really only three structures known.

Another significant breakthrough that has been made in our laboratory in the last two years is the process for partial fluorination of gas separation membranes. We have known from previous work that fluorination of polymer surfaces provides excellent gas diffusion barriers and liquid diffusion barriers. We reasoned that light fluorination of a selective gas separation membrane would change the selectivity in very pronounced ways. We have then tested this hypothesis on normal thin film membranes and soon hope to work on porous fiber (asymmetric) membranes. We have found that the selectivity increases especially for "size separation" systems are very large indeed (often after light fluorination the increase in selectivity is on the order of 10^3 !). These observations according to Professor Don Paul, a recognized authority in the field, constitute a major breakthrough in separation technology. This area of chemistry will also be a substantial part of our new program; it is now being developed jointly with Professor Donald Paul of The University of Texas Department of Chemical Engineering. A joint paper on this new phenomenon was recently published.⁸

In a system as simple as polyethylene, Figures 2 and 3 show a dramatic selectivity effect. First note that on Figure 2 the helium diffusion and hydrogen

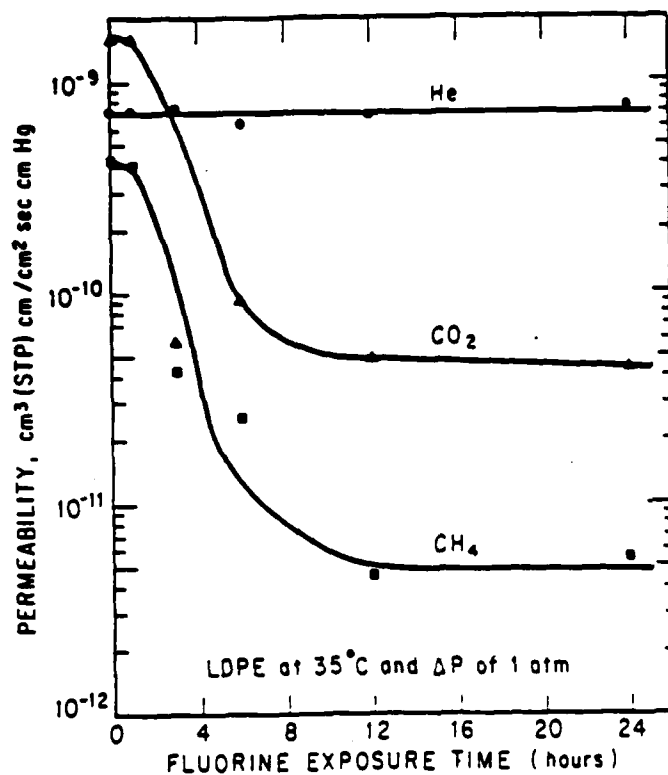


Figure 2

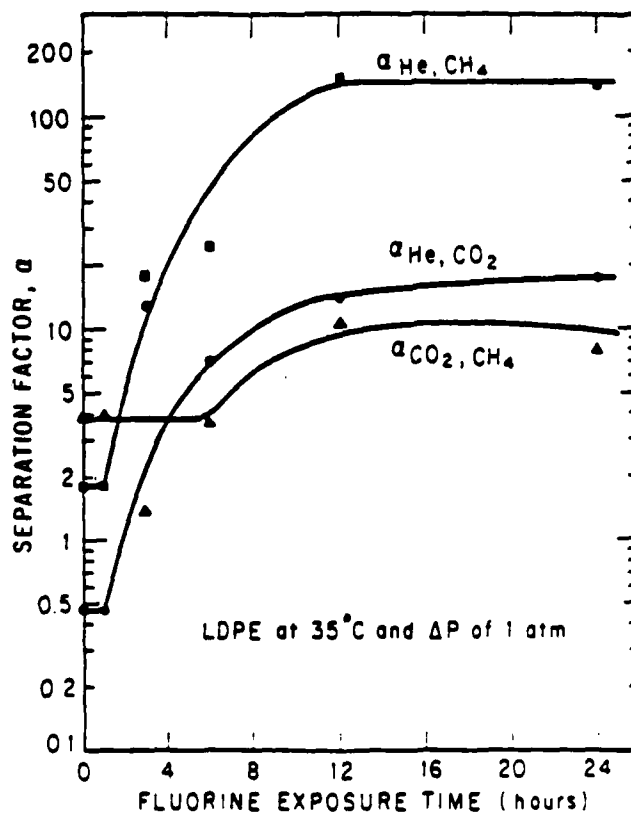
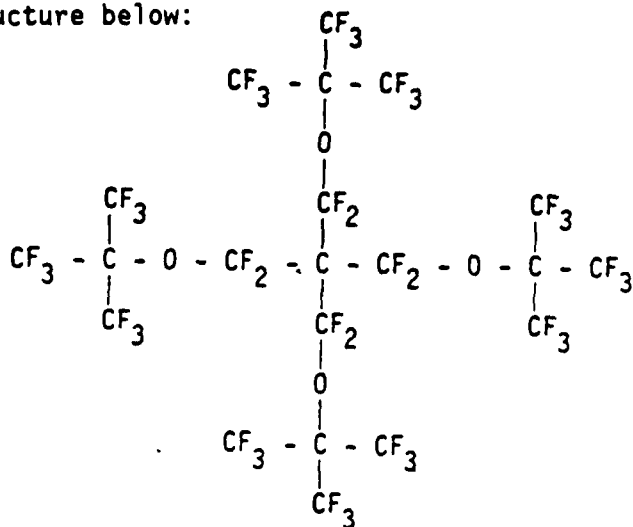


Figure 3

diffusion are completely unaltered, thus there is no drop off in flow rate whereas the permeability to carbon dioxide and methane are decreased by several orders of magnitude.

In our last proposal to AFOSR, we proposed synthesis of the highly branched perfluoropolyether structure below:

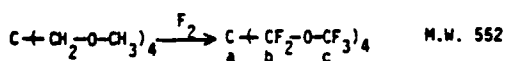


Perfluoro(pentaerythrityl tetra-t-butyl ether)

We did prepare some quantities of this and found that it was a rather viscous fluorocarbon grease. Perfluoropolyethers, it should be said, are very special materials because the ether linkage acts as a hinge. Therefore, many perfluoropolyethers have extraordinary low temperature properties. It just does not take very much thermal energy to produce some degree of vibrational energy in the ether linkage. There is also at very low temperatures free rotation about the ether linkage. For this reason well chosen perfluoropolyether structures will have excellent liquid properties at temperatures as low as -80° or -100°C . This also gives a small increase in the high temperature thermal stability since the ether linkage introduces considerable flexibility under thermal stress.

In the following pages one can see some of the structures that have very recently been synthesized in our laboratory:

PERFLUORO(PENTAERYTHRITYL TETRAMETHYL ETHER)



$^{13}C(^{19}F)$ and ^{19}F nmr data:

- a) 66.556
b) 119.363 -70.0 (relative to $CFCl_3$)
c) 117.282 -57.9

mass spectral data:

(P-F)	m/e 533
$C_7F_{13}O_3$	379
$C_7F_9O_2$	291
$C_5F_7O_2$	225
CF_3OCF_2	135 (base peak)
CF_3	69

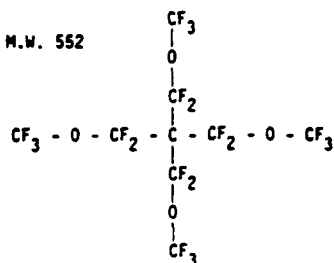
elemental analysis:

calc.	found
19.56% C	19.34
68.66 F	68.84
0.00 H	0.00
12.00 O	11.59

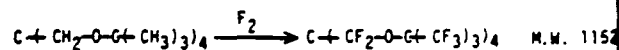
boiling point: 130.7°C

melting point -87.8°C

38% yield



PERFLUORO(PENTAERYTHRITYL TETRA-t-BUTYL ETHER)



^{19}F nmr data:

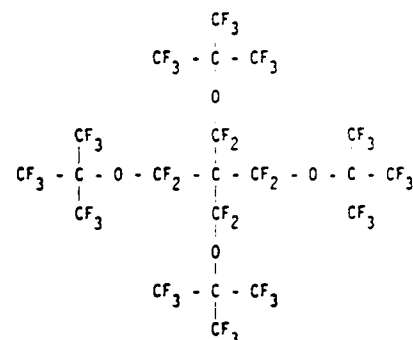
nmr shows a sharp singlet at -70.0 for CF_3
the CF_2 signal is an envelope of peaks centered at -130

mass spectral data:

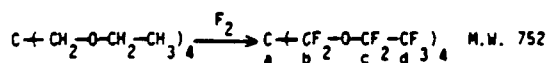
no (P-F) observed

shows regularly spaced peaks characteristic of polymerized material

material obtained is a viscous, very non-volatile oil



PERFLUORO(PENTAERYTHRITYL TETRAETHYL ETHER)



$^{13}C(^{19}F)$ and ^{19}F nmr data:

- a) 67.012
b) 118.453 -90.3 (relative to $CFCl_3$)
c) 116.047 -89.3
d) 114.356 -67.2

mass spectral data:

(P-F)	m/e 733	$CF_3CF_2OCF_2$	m/e 185
$C_9F_{17}O_3$	479	CF_3CF_2	119(base)
$C_7F_{11}O_3$	341	CF_3	69
$C_6F_9O_2$	275		

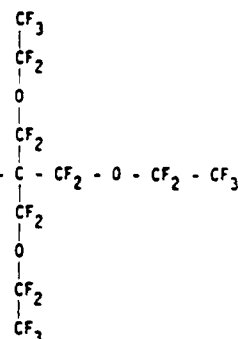
elemental analysis:

calc.	found
20.76% C	20.44
70.73 F	70.61
0.00 H	0.07
8.51 O	8.88

boiling point 170°C

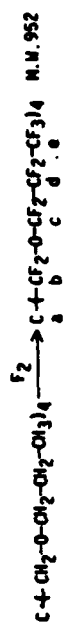
melting point -60°C

25% yield



PENTAFTHIRYL TETRAPROPYL ETHER

^{13}C (^{19}F) NMR OF PERFLUORO(PENTAERYTHRITYL TETRAPROPYL ETHER)



^{13}C (^{19}F) and ^{19}F nmr data:

a) 67.142	
b) 118.648	-85.5 (relative to CFCl_3)
c) 117.347	-83.3
d) 106.747	-131.0
e) 116.112	-66.5

mass spectral data:

no (P-F) observed	C_4F_7	m/e
$\text{C}_{13}\text{F}_{25}\text{O}_4$		695
$\text{C}_{12}\text{F}_{23}\text{O}_4$	$\text{CF}_3\text{CF}_2\text{CF}_2$	645
$\text{C}_8\text{F}_{13}\text{O}_3$	CF_3CF_2	391
$\text{CF}_3\text{CF}_2\text{CF}_2\text{OCF}_2$	CF_2CF_2	235
CF_3		69

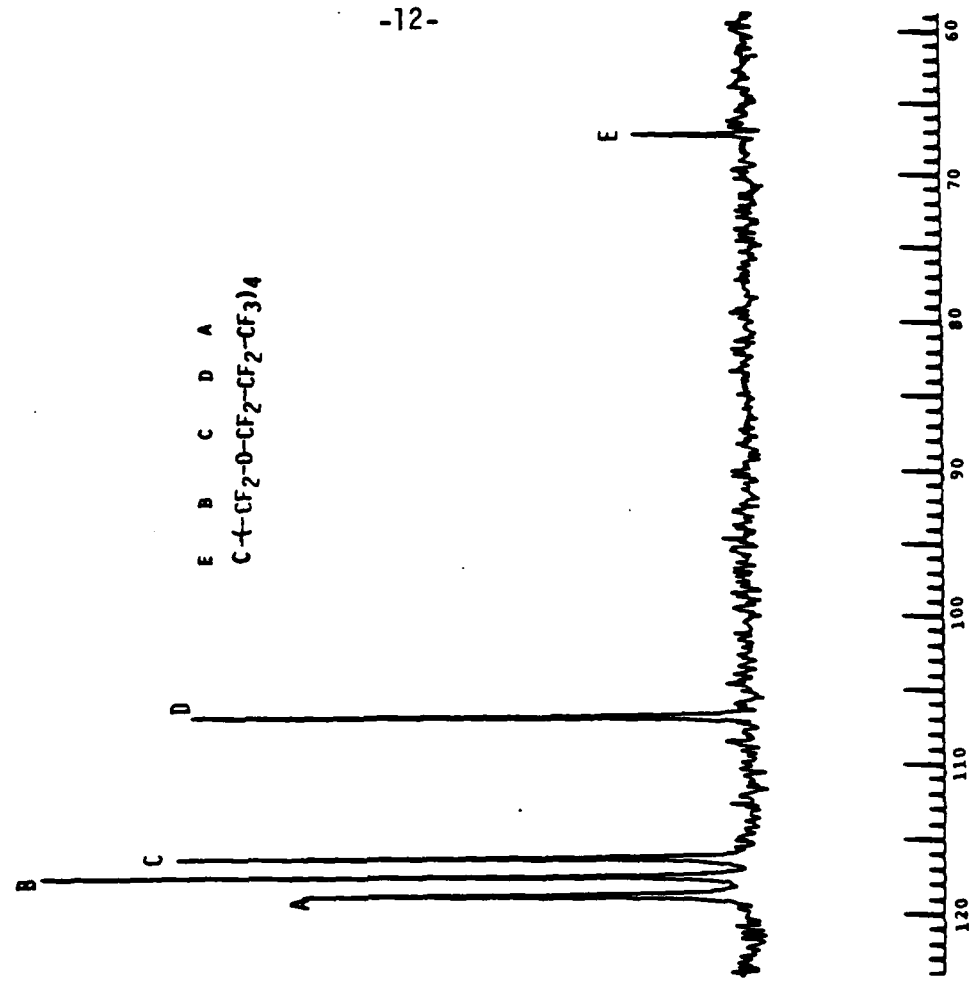
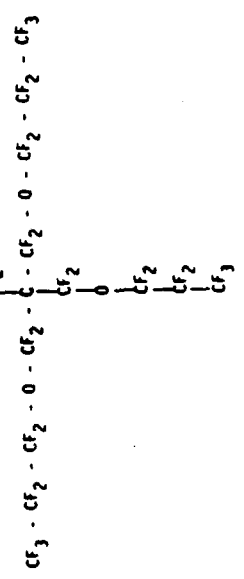
elemental analysis:

none to date

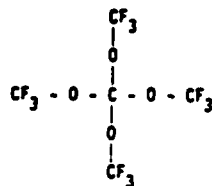
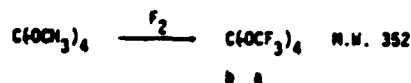
boiling point 232°C

melting point -54°C

31% yield



Further we have prepared what we believe is the first perfluoro ortho-carbonate:⁹



Boiling point 20.8°C
Melting point -45.0°C
Yield 49.5%

¹³C (¹⁹F) (vs. ext. (CH₃)₄Si) and ¹⁹F (vs. ext. CFCI₃) nmr data:

a) 118.6 ppm -59.0 ppm
b) 114.9 ppm

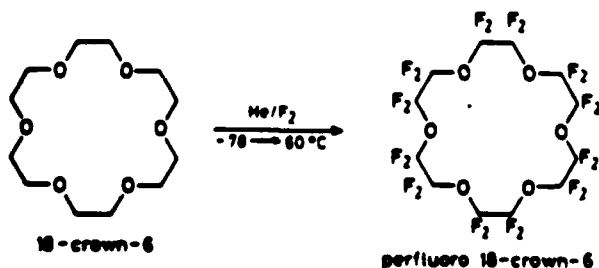
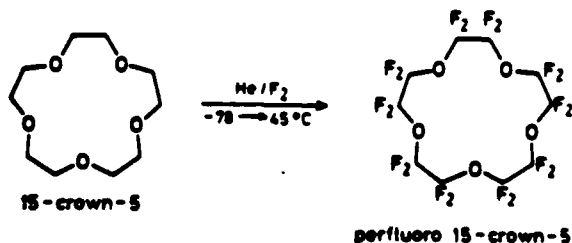
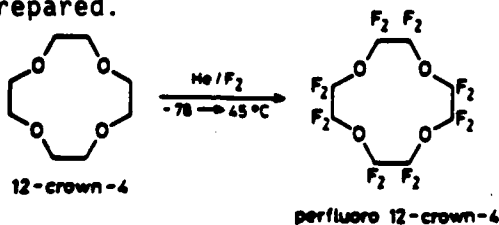
mass spectral data:

[P-OCF ₃] ⁺	267
[CF(OCF ₃) ₂] ⁺	201
[OCOCF ₃] ⁺	113
[OCF ₃] ⁺	85
[OCF] ⁺	47

elemental analysis:

calc.	found
17.05 C	
64.77 F	in process
0.00 H	
18.18 O	

Recently we published a manuscript on the first perfluoro crown ethers.¹⁰ Namely perfluoro 18-crown-6, perfluoro 15-crown-5, and perfluoro 12-crown-4 have been prepared.

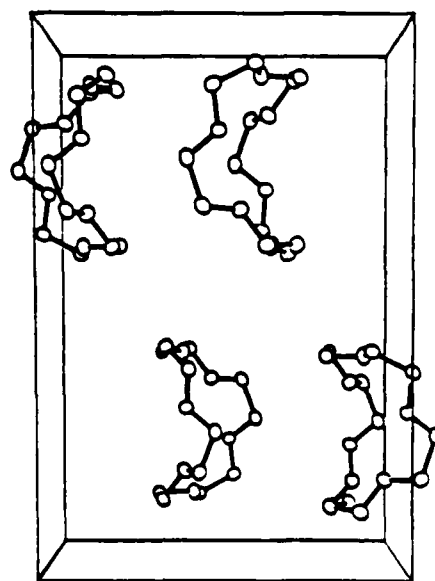
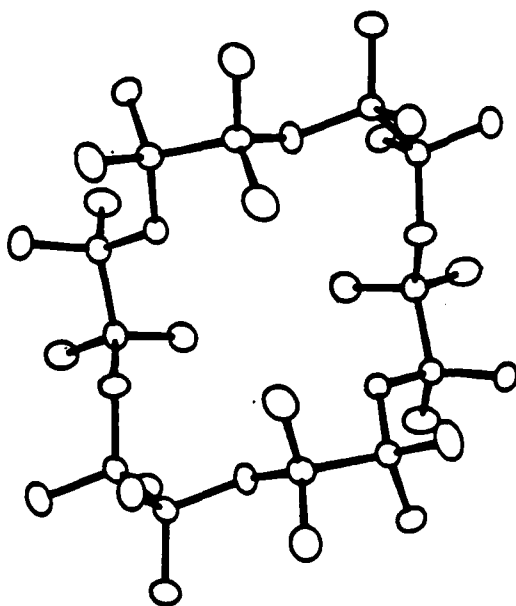


Properties and characterization of perfluoro 15-crown-5 and perfluoro 12-crown-4. Satisfactory elemental analyses (C, F) were obtained.

	15-crown-5	12-crown-4
Boiling point, °C	146	118
I.r. (vapour phase), cm ⁻¹	1250(s), 1228(vs), 1158(vs), 745(m)	1260(vs), 1188(vs), 1160(vs), 1080(m), 825(m), 745(br)
N.m.r. (neat liquid)	¹⁹ F -91.8(s) p.p.m. (ext. CFCI ₃) ¹³ C δ 114.9 (s)	¹⁹ F -90.0(s) p.p.m. (ext. CFCI ₃) ¹³ C δ 114.9 (s)
Mass spectrum, m/z	580 (C ₁₀ F ₂₀ O ₄ , M ⁺)	445 (C ₈ F ₁₆ O ₄ , M ⁺ - F)

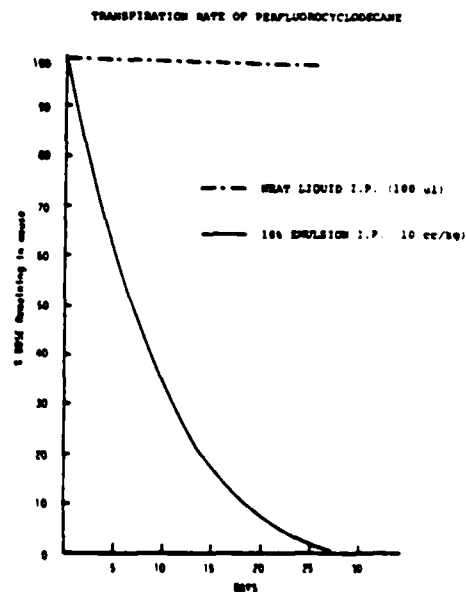
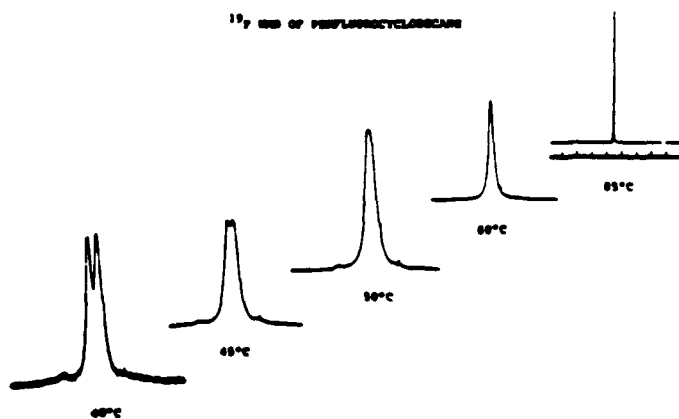
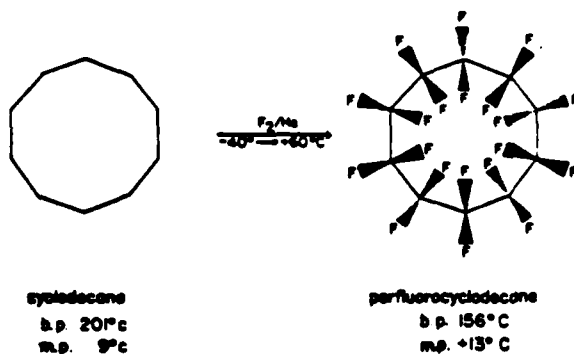
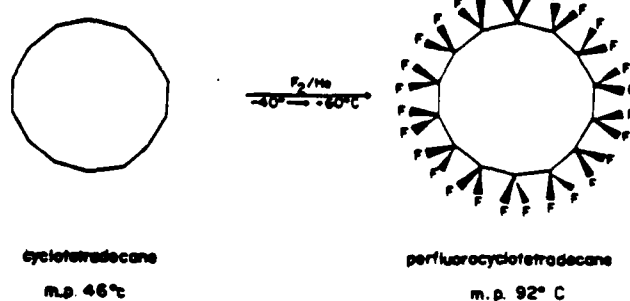
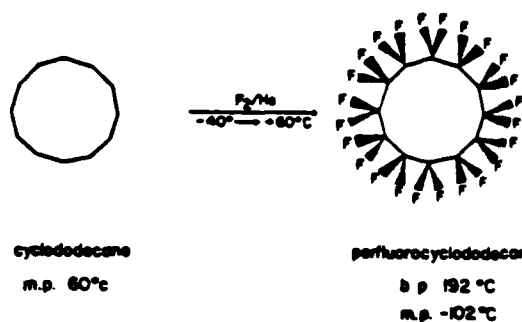
* A table for the straight-chain fragmentation products listing mass spectral and ¹⁹F data (two pages) is available from the authors

This work by Wen-Huey Lin of our research group has produced some really interesting and thermally stable fluorocarbons. The perfluoro crown ethers are much weaker bases than crown ethers. We already know of a number of potential applications for the materials. As far as coordinating cations, we are doing some collaborative work with Dr. Barry Haymore of Monsanto. We have succeeded in showing that we can at least clatherate the potassium ion in 18-crown-6. The perfluoro compounds 15-crown-5 and 12-crown-4 are nontoxic extremely stable liquids whereas perfluoro 18-crown-6 is amazing in its physical appearance. It forms beautiful crystals in sealed tubes often weighing as much as half a gram. These single crystals have an appearance very similar to zircons, material commonly used for sparkling costume jewelry. The structure of perfluoro 18-crown-6 has been done and is a feature of a second full paper about to emerge.¹¹



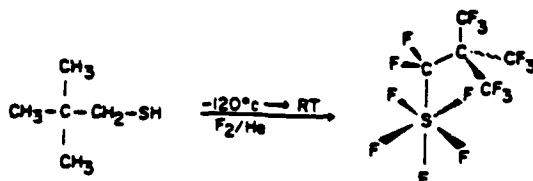
The 18-crown-6 structure is considerably less planar than the hydrocarbon structure.

The success that we had with the perfluoro crown ethers has also led us to look for other systems that would have somewhat similar properties. Previously perfluoro cyclooctane was prepared by elemental fluorine reactions in our research program.¹² Thus a very able member of our research group, Hsu-Nan Huang, prepared a number of unknown cyclic fluorocarbons and they too have applications in the fluorocarbon biomedical area and licensing possibilities are under discussion for these as well.¹³



Note also in the figure above that there are some really interesting temperature dependent NMR phenomena associated with the new species where nonequivalent fluorine are observed until the ring compounds are heated and there is rapid ring equilibration. The structures of these species are being obtained in collaboration with the Simonsen crystallography group at the University of Texas.

Another area of active interest recently in our research program has been the synthesis of organofluorine sulfur compounds. One of the most spectacular of these recently prepared is the species, perfluoroneopentyl sulfur pentafluoride which we obtained in high yield from the mercaptan.¹⁴ We are in hope that this will also be a dielectric material such as SF₆. Its boiling point is 108°C and melting point -87°C. We are very interested in the structure of this material.



neopentyl mercaptan

perfluoroneopentyl sulfur pentafluoride

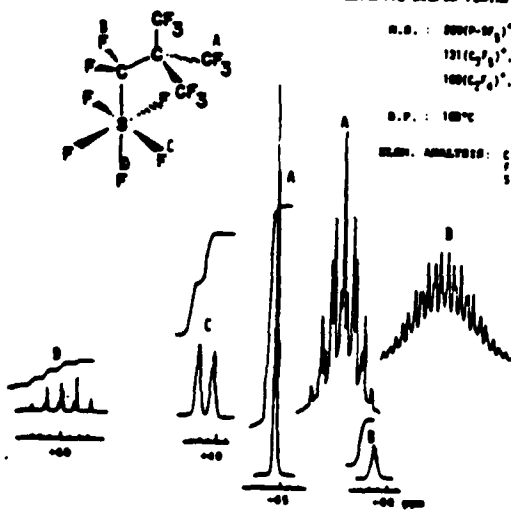
71.0%
yield (24.5%)
b.p. 108°C
m.p. -87°C

¹⁹F NMR OF PERFLUORONEOPENTYL SULFUR PENTAFLUORIDE

h.f. : 280(M-SF₆)⁺, 101(C₂F₅)⁺, 100(C₂F₆)⁺,
131(C₂F₅)⁺, 127(SF₆)⁺, 100(SF₆)⁺,
100(C₂F₆)⁺, 99(C₂F₅)⁺, 99(SF₆)⁺, 99(C₂)⁺

b.p. : 108°C

elem. analysis: C 18.20% (18.10%)
F 76.74% (76.77%)
S 0.06% (0.09%)

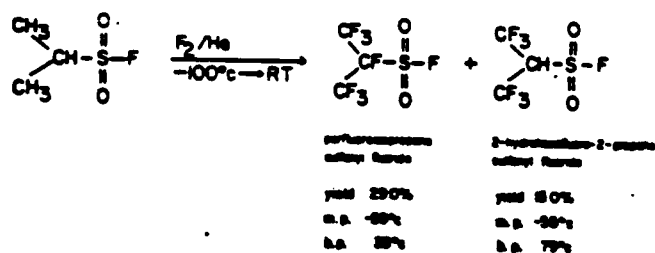


¹³C(125p) NMR OF PERFLUORONEOPENTYL SULFUR PENTAFLUORIDE

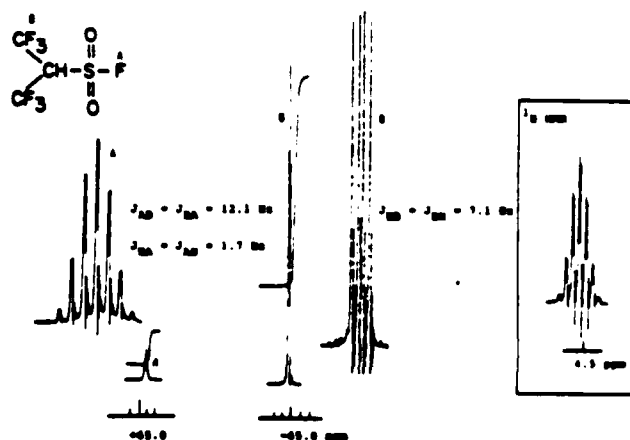


On the next pages you will see a number of other sulfur fluorine carbon compounds which were made for various reasons recently. Some of these have such interesting structures where the syntheses should be of definite interest to reviewers who have a background and interest in organosulfur fluorine chemistry. Some are starting materials for new fluorocarbon functional membranes. Ten other organofluorine structures are in the process of being fully characterized.

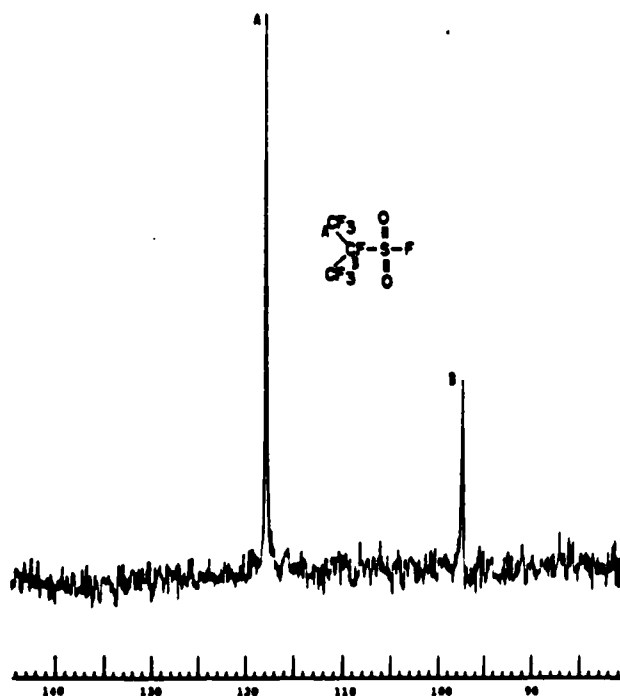
Direct Fluorination of Isopropanesulfonyl Fluoride



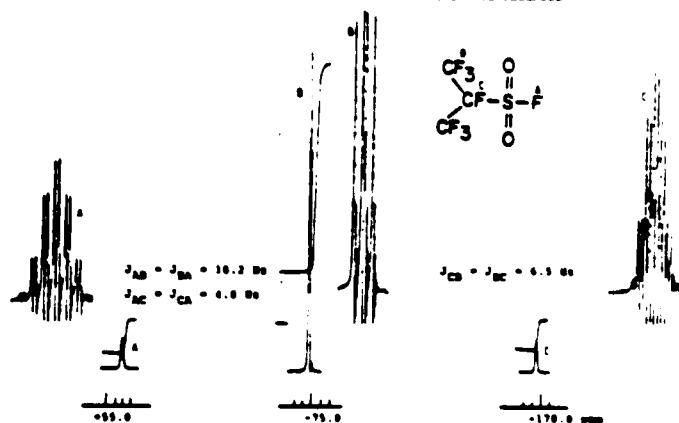
¹⁹F and ¹³C NMR OF 2-(TRIFLUOROMETHYL)-2-PROPANE SULFONYL FLUORIDE



¹³C(100) NMR OF PERFLUOROPROPANE SULFONYL FLUORIDE

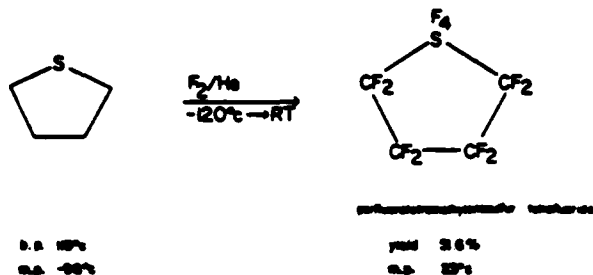


¹⁹F NMR OF PERFLUOROPROPANE SULFONYL FLUORIDE

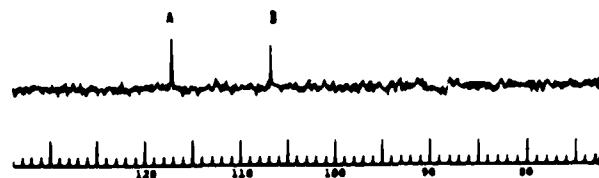
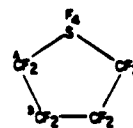


Direct Fluorination of Tetramethylene sulfide

$^{13}\text{C}(^{19}\text{F})$ NMR OF PERFLUOROTETRAMETHYLENE SULFIDE

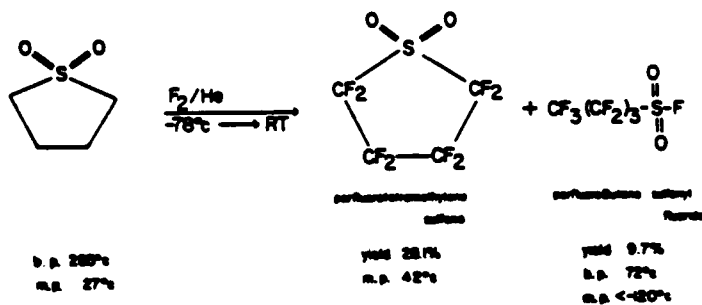


b.p. 15°C
m.p. -98°C

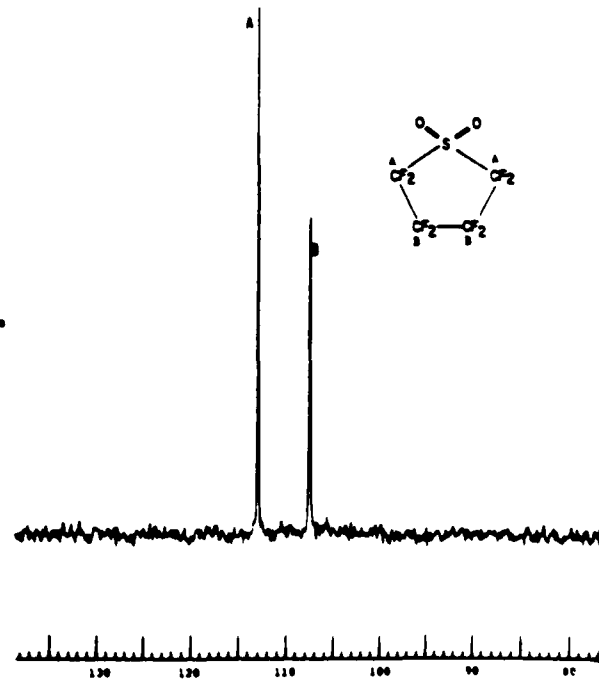
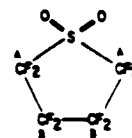


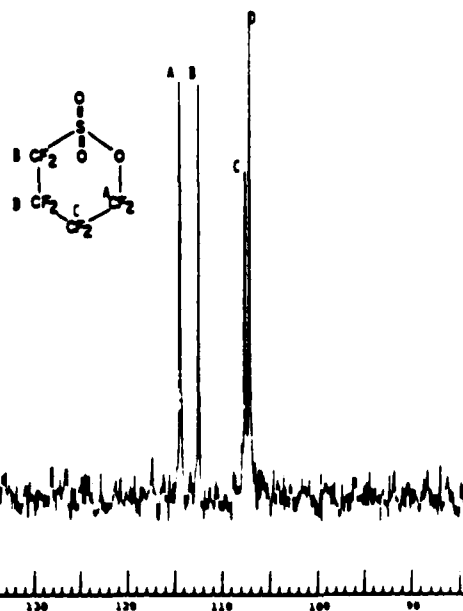
Direct Fluorination of Tetramethylene sulfone

$^{13}\text{C}(^{19}\text{F})$ NMR OF PERFLUOROTETRAMETHYLENE SULFONE

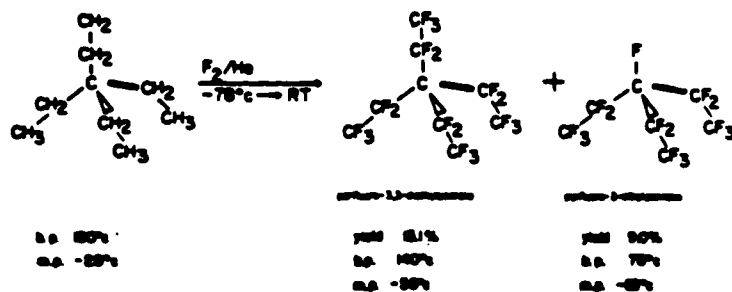


b.p. 280°C
m.p. 27°C

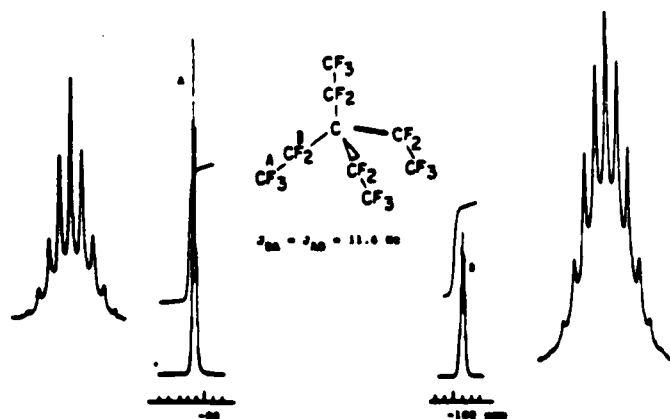




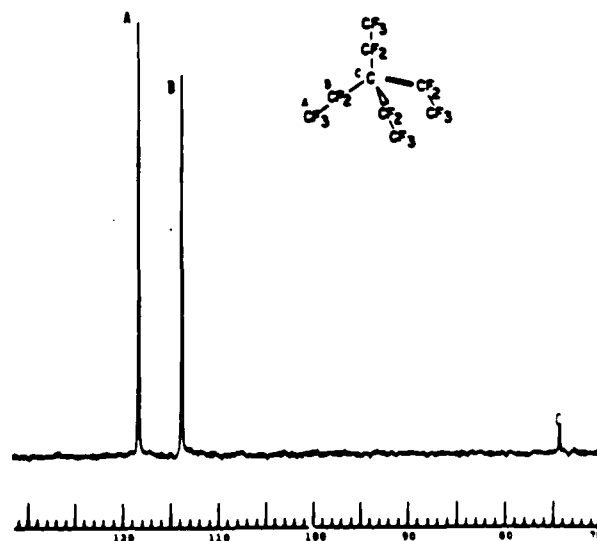
We have had a long and continuing interest in highly branched fluorocarbons. One very interesting compounds just prepared is perfluoro-3,3-diethylpentane (a perfluoroneopentane analogue).



¹⁹ See, e.g., FOIA-2000-1, 2-SUBMITTANCE



13C(18P) was 07 FEBRUARY-1.1-010000-000000



We have some preliminary results as well on the propyl and butyl four coordinate carbon species.¹⁵ It does appear that we may be able to synthesize both of those compounds as well as produce some highly interesting fragment materials from the breakage of only one of the chains while the very sterically hindered molecules undergo fluorine substitution.

Professor Richard J. Lagow

Recent Publications Arising from Air Force Office of
Scientific Research Grant #AFOSR-82-0197

1. "The Direct Fluorination of Hexamethyldigermene and Hexamethyldisilane," Inorg. Chem., 21, 524 (1982) (with R.E. Aikman).
2. "The Synthesis of Tetrakis(perfluorocyclohexyl)methane and Bis(perfluorocyclohexyl)difluoromethane by Direct Fluorination," J. Org. Chem., 47, 2789 (1982) (with R.E. Aikman).
3. "A New Synthesis of Trifluoromethylthio Organometallic Compounds by Low Temperature Cocondensation of Trifluoromethylthio Radicals and Metal Vapor," Inorg. Chem., 22, 359 (1983) (with T.R. Bierschenk).
4. "A New Synthesis for Methyl/Trifluoromethyl Organometallic Compounds by Low Temperature Cocondensation of Trifluoromethyl Radicals and Main Group Methyls," J. Organomet. Chem., 254, 53 (1983) (with M.A. Guerra, R.L. Armstrong and W.I. Bailey, Jr.).
5. "Metal Vapor Synthesis of Trifluoromethyl-Group III Compounds," J. Organomet. Chem., 277, 1 (1984) (with T.R. Bierschenk, T.J. Juhlke and W.I. Bailey, Jr.).
6. "The Synthesis of Perfluorinated Polyethers Via Polyesters Deriving From Hydrocarbons. A General Method," Makromol. Chem., Rapid Commun., 6, 85 (1985) (with D.F. Persico and G.E. Gerhardt).
7. "The Synthesis of Perfluoropolyethers Via Hydrocarbon Polyesters: A New General Method," J. Am. Chem. Soc., 107, 1197 (1985) (with D.F. Persico and G.E. Gerhardt).
8. "Synthesis of Branched Perfluoroethers By Direct Fluorination; Copolymers Based on Hexafluoroacetone," Macromolecules, 18, 1383 (1985) (with D.F. Persico).
9. "The First Perfluoro Crown Ethers," J. Chem. Soc., Chem. Commun., 19, 1350 (1985) (with W.H. Lin and W.I. Bailey, Jr.).
10. "A General Synthesis for Symmetrical Highly Branched Perfluoroethers; A New Class of Oxygen Carriers," J. Org. Chem., 50, 5156 (1985) (with D.F. Persico, H.N. Huang and L.C. Clark, Jr.).
11. "The Generality of Metal Atom-Free Radical Reactions and Synthesis of New Trifluoromethyl Alkyls of Gold III and Silver," J. Organomet. Chem., 307, C58 (1986) (with M.A. Guerra and T.R. Bierschenk).
12. "Group IIB Metal Alkyls: The Synthesis and Stabilization of Trifluorosilyl and Trifluoromethyl Alkyls of Cadmium and Zinc," J. Am. Chem. Soc., 108, 4103 (1986) (with M.A. Guerra and T.R. Bierschenk).

13. "Gas Transport in Partially Fluorinating Low Density Polyethylene," J. Appl. Polym. Sci., 31, 2617 (1986) (with C.L. Kiplinger, D.F. Persico and D.R. Paul).
14. "Bis(trifluorosilyl)mercury, Bis(trifluoromethyl)mercury and Bis(trifluoromethyl)tris(trimethylphosphine)nickel," Organometallic Syntheses, 3, 426 (1986) (with T.R. Bierschenk and W.I. Bailey, Jr.).
15. "High Yield Reactions of Elemental Fluorine," J. Fluorine Chem., 33, 321 (1986).
16. "Synthesis of New High Molecular Weight Cyclic Fluorocarbons and Highly Branched Fluorocarbons Such as Perfluoro-3,3-Diethylpentane," Bull. Soc. Chim. Fr., 6, 993 (1986) (with H.N. Huang).
17. "Further Developments of the Metal Vapor/Alkyl Radical Reaction. Synthesis of Tris(trifluoromethyl)indium and Bis(trifluorosilyl)cobalt and Their Base Adducts," Revue de Chimie Minerale, 23, 701 (1986) (with M.A. Guerra and T.R. Bierschenk).
18. "The Synthesis and X-ray Crystal Structures of $[\text{Au}(\text{CH}_2)_2\text{PPh}_2]_2(\text{CF}_3)_2$, $[\text{Au}(\text{CH}_2)_2\text{PPh}_2]_2(\text{C}_6\text{F}_5)_2$ and $[\text{PPN}][\text{Au}(\text{C}_6\text{F}_5)_4]$: Two Dinuclear Gold(II) Ylide Complexes Containing Alkyl and Aryl Ligands and the First Example of a Homoleptic Au(III) Pentafluorophenyl Complex," Inorg. Chem., 26, 357 (1987) (with H.H. Murray, J.P. Fackler, Jr., L.C. Porter, D.A. Briggs and M.A. Guerra).
19. "Synthesis of Trifluorosilyl Organometallic Complexes From Trifluorosilyl Radicals and Metal Atoms," J. Am. Chem. Soc., in press (with T.R. Bierschenk, M.A. Guerra, T.J. Juhlke and S.B. Larson).

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3. G.E. Gerhardt, E.T. Dumitru and R.J. Lagow, J. Polym. Sci., Polym. Chem. Ed., 18, 157 (1979).
4. D.F. Persico, G.E. Gerhardt and R.J. Lagow, J. Am. Chem. Soc., 107, 1197 (1985).
5. (a) W.R. Hasek, W.C. Smith and V.A. Englehardt, J. Am. Chem. Soc., 82, 543 (1960); (b) W.C. Smith, Angew. Chem., Int. Ed. Engl., 1, 467 (1962).
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12. N.J. Maraschin, B.D. Catsikis, L.H. Davis, G. Jarvinen and R.J. Lagow, J. Am. Chem. Soc., 97, 513 (1975).
13. H.N. Huang and R.J. Lagow, in preparation.
14. H.N. Huang and R.J. Lagow, in preparation.
15. H.N. Huang and R.J. Lagow, Bull. Soc. Chim. Fr., 6, 993 (1986).

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